

Fig. 37.2. Generalized overall refinery from crude oil to salable products. (American Petroleum Institute.)

Common refinery fractions are:

| | | |
|---|--|---|
| <i>Natural</i> (or casing-head) gasoline and natural gas | <i>Intermediate distillates</i> Heavy fuel oils | Waxes (candles, sealing, paper treating, insulating) |
| LPG | Diesel oils | <i>Residues</i> |
| <i>Light distillates</i> | Gas oils | Lubricating oils |
| Motor gasolines | <i>Heavy distillates</i> | Fuel oils |
| Solvent naphthas | Heavy mineral oils (medicinal) | Petrolatum |
| Jet fuel | Heavy flotation oils | Road oils |
| Kerosene | Lubricating oils | Asphalts |
| Light heating oils | | Coke |

Natural gas (Chap. 6) occurs as accumulations in porous, underground reservoirs with or without accompanying crude. Natural gas was discovered in the United States in the early 1800s, although it had been known elsewhere for centuries. For a time, much natural gas was wasted, but now it is a most important fuel and petrochemical feedstock. "Wet" gas contains vapors of hydrocarbons in the gasoline boiling range, and at one time was simply stripped of its gasoline content, then wasted. The condensed liquid obtained from wet gas is commonly known as natural gasoline. Gas reserves are being discovered at a greater rate than gas consumption. The free world reserves are now (1982) estimated at $48.8 \times 10^{12} \text{ m}^3$. This is a 49-year supply¹⁷ at 1981 production rates. In 1981 $1.6 \times 10^{12} \text{ m}^3$ was added to the reserve; consumption was $1.03 \times 10^{12} \text{ m}^3$. Natural gas is composed chiefly of paraffin series hydrocarbons from C_1 through C_5 with CO_2 , N_2 , and sometimes He as diluents. The most important products obtained from natural gas are fuel, LNG (liquefied natural gas), natural gasoline, carbon black, helium, hydrogen, synthesis gas, and many petrochemicals.

NATURAL GAS LIQUIDS. Gasoline condensed from natural gas contains fewer high-boiling constituents than that obtained from straight-run refining of crude and is, therefore, considerably more volatile. The term natural,¹⁸ or casinghead, gasoline is applied as a special name to distinguish it. While the antiknock properties are only fair, the volatility makes natural gasoline desirable for blending into fuels for use in winter. High volatility makes for easy starting.

Gas withdrawn from underground reservoirs under pressure carries with it lighter components vaporized from the crude oil with which it has been in contact. The composition of the natural gas liquids obtained by condensing these components is determined in large degree by the composition of the crude. Natural gasoline and natural gas liquids are now major petrochemical feedstocks. Isomerization of natural gasoline produces large quantities of isobutane and isopentane which are then reacted with light olefins such as butylene to furnish high antiknock alkylated gasoline.

Because of the demand for high-octane (antiknock) fuel, readily made from natural gas liquids, and of the continuing demand for petrochemical feedstocks, essentially all natural gas is stripped of its condensable material. The individual components are separated by (1) refrigerated absorption, (2) low-temperature distillation, (3) adsorption, or (4) one of the new membrane separation processes. A refrigeration process designed to separate ethane, propane, and natural gas with a high (80+ percent) percentage of the ethane recovered is shown in

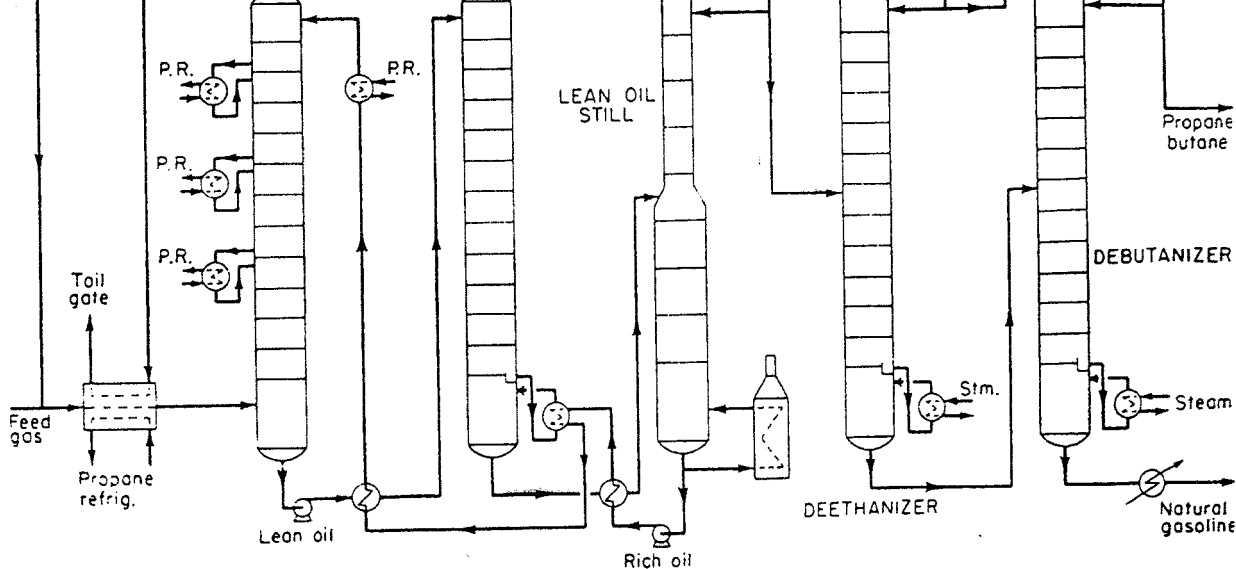
¹⁷World Energy Outlook, op. cit.

¹⁸Campbell, *Gas Conditioning and Processing*, 4th ed., 2 vols., Petroleum Publ. Co., Tulsa Okla., 1976.

Refinery Gases. The highest volume of gases generated in the refinery by decomposition of crudes comes from the cracking units. Unlike natural gas, these contain significant proportions of olefins. If temperatures and pressures are kept low, these can be collected and used to make petrochemicals. The separation processes are similar to those for natural gas liquids.

The diagram illustrates a chemical process involving two main units: an **ABSORBER** and a **DEMETHANIZER**.

- ABSORBER:** A vertical vessel where a gas stream enters from the bottom and a liquid stream enters from the top. The gas stream is labeled **Ethane** at its inlet. The liquid stream is labeled **P.R.** (Process Recycle) at its inlet. The gas outlet is at the top, and the liquid outlet is at the bottom.
- DEMETHANIZER:** A vertical vessel where a gas stream enters from the bottom and a liquid stream enters from the top. The gas outlet is at the top, and the liquid outlet is at the bottom.
- Streams:**
 - Gas Stream:** Enters the absorber from the bottom, goes to the demethanizer, and returns to the absorber from the top.
 - Liquid Stream:** Enters the absorber from the top, goes to the demethanizer, and returns to the absorber from the bottom.
- Components:** The diagram includes two vertical vessels (absorber and demethanizer), two horizontal vessels (likely storage or intermediate processing), and two pumps (indicated by circles with diagonal lines) to move the liquid stream between the vessels.



| | | | |
|------------------------|--|-----------------|--------------------------|
| Natural gas feed | 2.83×10^7 std m ³ /day | Cooling water | 19 m ³ /min |
| Lean oil (100 mol. wt) | 38 m ³ /min | Operating labor | 60 work-h/day |
| Fuel gas | 8.49×10^5 std m ³ /day | Liquid products | 1.32×10^7 L/day |
| Electrical power | 25,200 MJ | | |

Fig. 37.3. Natural gas plant (high-ethane recovery) operated by absorption and propane refrigeration.
(M. W. Kellogg Co.)

PRODUCTS OF REFINING

Precursors of Petrochemicals

As markets change, there is constant alteration in the materials used for the manufacture of petrochemicals. Almost any synthesis desired can be brought about; the problem is to do it at low cost with the equipment available. Table 37.5 shows the unit operations involved. In earlier times, acetylene was used extensively for making petrochemicals, but it is difficult to make and store, so ethylene has now become the principal raw material for further synthesis.¹⁹ Precursors are reactive materials usually made by breaking down larger molecules, called feedstocks. Ethylene is currently being made from LNG, naphtha, gas oil, diesel fuel, ethane, propane, and butane, with coal a possibility soon to be explored, and some testing of liquefied coal already completed. The principal precursors are:

| | | | |
|-----------|-----------|---------|-------------|
| Acetylene | Propylene | Benzene | Xylenes |
| Ethylene | Butene | Toluene | Naphthalene |

Acetylene production is covered in Chap. 7.

The manufacture of *ethylene* from distillates, natural gas, or gas liquids is shown in the generalized flowchart of Fig. 37.4. This is the largest volume organic material. The conditions for its manufacture lie somewhere between those usually thought of as refining and those encountered in chemical production. Extremely large plants are built and being built. Some plants have a production capacity as large as 7×10^8 kg/year. In 1980, 57 percent of ethylene

¹⁹Kniel, Winter, and Stork, *Ethylene—Keystone to the Petrochemical Industry*, Marcel Dekker, New York, 1980; Brumm, How Will They Feed the Ethylene Plants of the 1990's? *Chem. Bus.*, October 20, 1980, p. 19.

Table 37.5 Unit Operations for Separation of Olefins and Aromatics as Precursors of Petrochemicals

| Operation | Based on Differences In: | Product |
|--------------------------------|----------------------------|---|
| <i>Vapor-Liquid</i> | | |
| Distillation | Vapor pressure | Ethylene from ethane |
| Extractive distillation | Polarizability | <i>n</i> -Butenes from butanes |
| Azeotropic distillation | Polarizability | Toluene from aromatics |
| Absorption | Solubility | Ethane from methane |
| <i>Liquid-Liquid</i> | | |
| Solvent extraction | Solubility | Benzene from aliphatics |
| <i>Liquid-Solid</i> | | |
| Crystallization | Melting point | <i>p</i> -from other xylene |
| Extractive crystallization | Clathrate* formation | <i>n</i> -Paraffins from other hydrocarbons |
| Encapsulation | Clathrate formation | <i>m</i> -Xylene |
| Adsorption on molecular sieves | Surface or pore adsorption | <i>n</i> -Paraffins from isoparaffins |
| <i>Vapor-Solid</i> | | |
| Adsorption on molecular sieves | Surface or pore adsorption | Ethylene from ethane |

*Clathrates separate primarily on molecular size and shape.

NOTE: In addition to the physical property differentials tabulated here, chemical differentials are employed, e.g., reversible chemical reaction rates or chemical equilibriums, as exemplified by separating pure butadiene from butene, using reaction with cuprous salts.

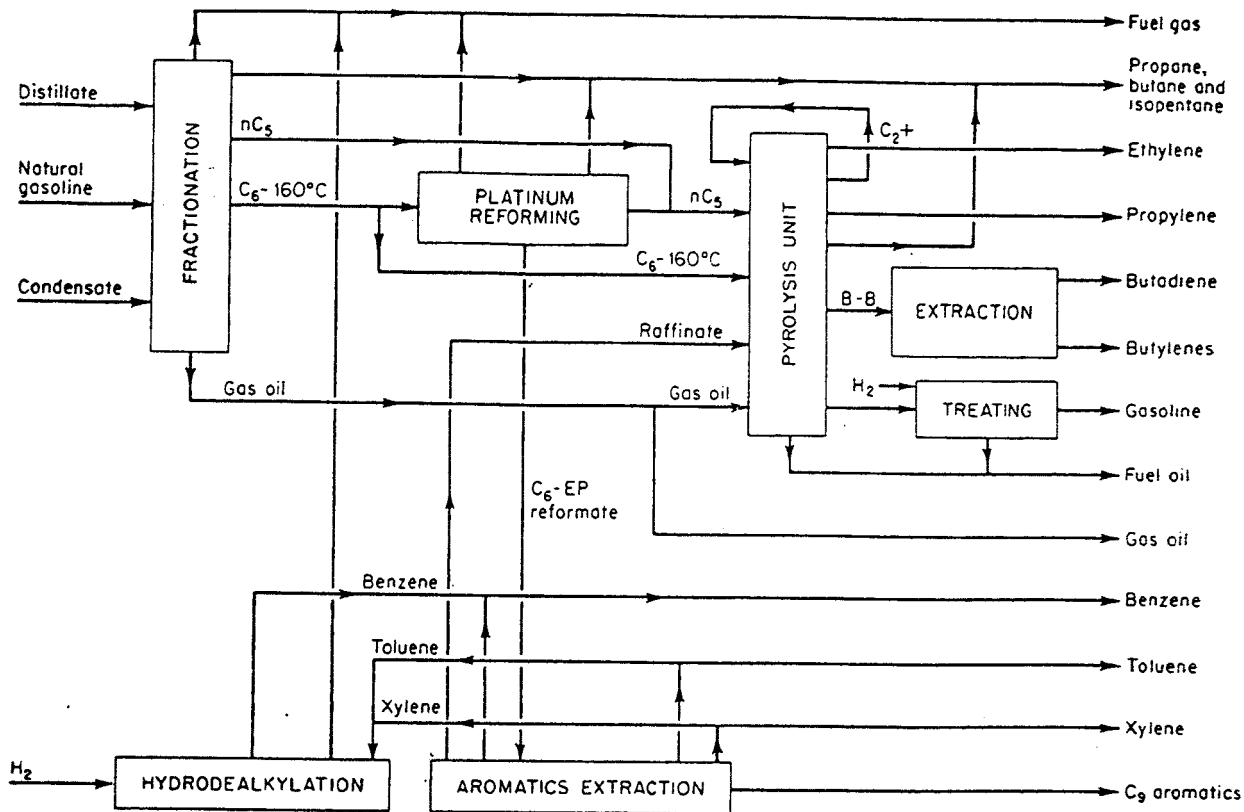


Fig. 37.4. Generalized flowchart for the production of petrochemicals. (M. W. Kellogg Co.)

production was based on NGLs; by 1990 the feed is expected to be 60% light hydrocarbons and 40% refinery products.²⁰ The material to be processed (cracked) is diluted with an inert gas (usually steam) at around 925°C with a residence time of 30 to 100 ms which yields a mixed product which must be separated to be useful. The gases are rapidly quenched, chilled, dehydrated, and fractionated to yield high-purity individual components and unwanted material for recycling. Changing feedstocks and conditions alter the product composition, e.g., butylene or propylene could be made the primary product, if desired. The flowchart of Fig. 37.5 shows the manufacture from refinery gas with the analysis (in percent): methane,

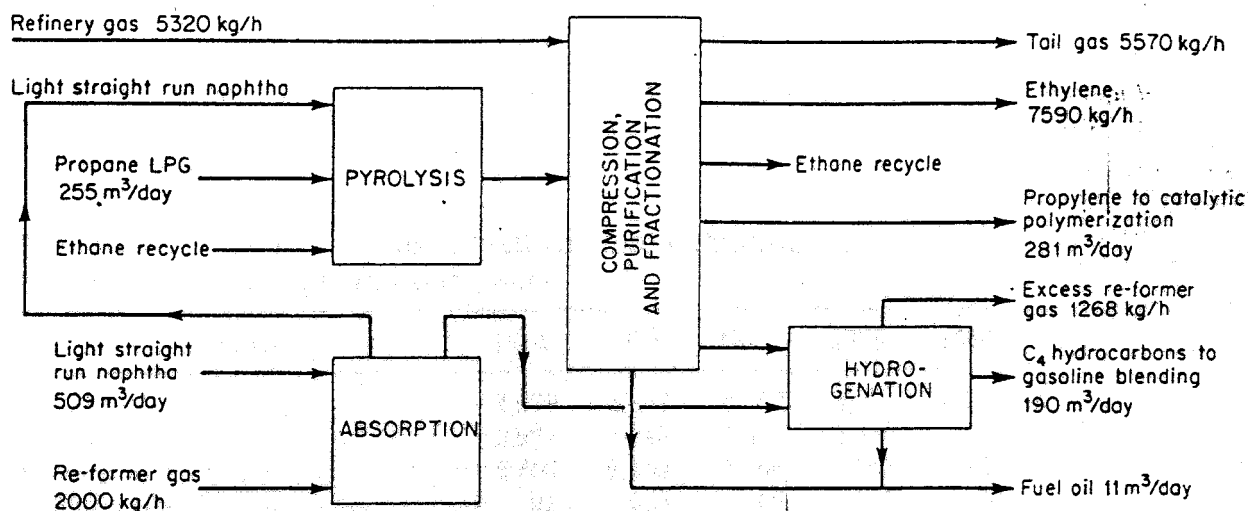
²⁰Kniel, op. cit.

Fig. 37.5. Flowchart for ethylene and propylene production from refinery gas. (Chem. Eng. and M. W. Kellogg Co.)

25; hydrogen, 19; ethane, 15; ethylene, 7; propane, 12; and propylene, 6, with the remainder N_2 , CO, CO_2 , H_2S , and higher hydrocarbons. LPG, high-run gasoline, and ethylene recycle may be added to this. Ethylene production in 1982 was 13.6×10^9 kg/year, but plant capacity was 18.6×10^9 kg/year. Much of the idle capacity was designed for naphtha or gas oil feed, which have become more expensive than light hydrocarbons as a source of ethylene.

A high-severity short-time crack of naphtha feedstock yielded²¹ a mix containing (in percent): hydrogen, 1.2; methane, 15.2; acetylene, 1.3; ethylene, 31.8; ethane, 1.2; propadiene, 1.2; propylene, 11.6; propane, 0.3; butadiene, 4.7; butylene, 2.2; and C_{5+} liquids, 27.7.

The increasing cost of light feedstocks and the demand for naphthas for other uses have caused increasing attention²² to be paid to heavier fractions such as vacuum gas oils, which have become a glut on the market. Both in the United States and abroad, extensive experiments have shown that the production of olefins from such heavy feedstocks, even heavy crude, is possible and will take place when economic conditions warrant it.

*Propylene*²³ is rarely produced except as a coproduct with ethylene. Steam cracking of ethylene produces most of it, and virtually all of it is used for polymer production. The remainder, used mostly for chemical production, comes from oil refinery fluid catalytic crackers. Refinery propylene is used mainly for alkylation. Production in 1982 was 7.3×10^9 kg/year with a plant capacity of 10.4×10^9 kg/year.

Aromatics are usually thought of as coal-derived, but the amount from that source in 1980 was almost vanishingly small, 4 percent of the benzene, 0.9 percent of the toluene, and only 0.1 percent of the xylenes. Table 37.6 gives statistics for U.S. production, and Fig. 37.6 shows the interrelation between uses and sources. Benzene can be made by *dehydrogenation* of cyclohexane or substituted cyclohexanes, by *aromatization* of methylcyclopentane, and by *demethylation* of toluene or xylenes. The demand for aromatics is large and attention is being given to find catalysts to produce more BTX (benzene-toluene-xylene) for chemical and high-grade fuel use. Toluene is recoverable, as such, from a few stocks, but most is made by dehydrogenation of naphtha; e.g., methylcyclohexane is dehydrogenated to toluene. This can then be demethylated to benzene, if desired.

Naphthalene is used in smaller quantities than the lighter aromatics, but with 2×10^7 kg used in 1981, its consumption is far from trivial. Six U.S. plants have a combined capacity of

²¹Prescott, Pyrolysis Furnace Boosts the Ethylene Yield by 10–20%, *Chem. Eng.* 82 (14) 52 (1975).

²²Baldwin and Kamm, ACR Process for Ethylene, *Chem. Eng. Prog.* 79 (1) 68 (1983); Fujita et al., Olefins from Heavy Oils, *Chem. Eng. Prog.* 79 (1) 76 (1983).

²³Spitz, Propylene—Key Question of the Future, *Chem. Eng. Prog.* 71 (11) 13 (1976).

Table 37.6 U.S. Petroleum-Based Aromatic Production
(in millions of kilograms per year)

| Product | 1974 | 1976 | 1977 | 1978 | 1980 |
|--------------------------------|--------|--------|--------|--------|--------|
| Benzene | 4,679 | 4,467 | 4,562 | 4,774 | 6,510 |
| Toluene | 2,977 | 3,245 | 3,317 | 3,428 | 3,308 |
| Xylenes | 2,760 | 2,489 | 2,796 | 2,915 | 3,134 |
| Naphthalene | 91 | 255 | 69 | 71 | 46 |
| Other aromatics and naphthenes | 1,551 | 1,991 | 1,434 | 1,874 | 1,815 |
| Grand total | 12,058 | 12,447 | 12,178 | 13,062 | 14,813 |

From data of the U.S. International Trade Commission, annually.

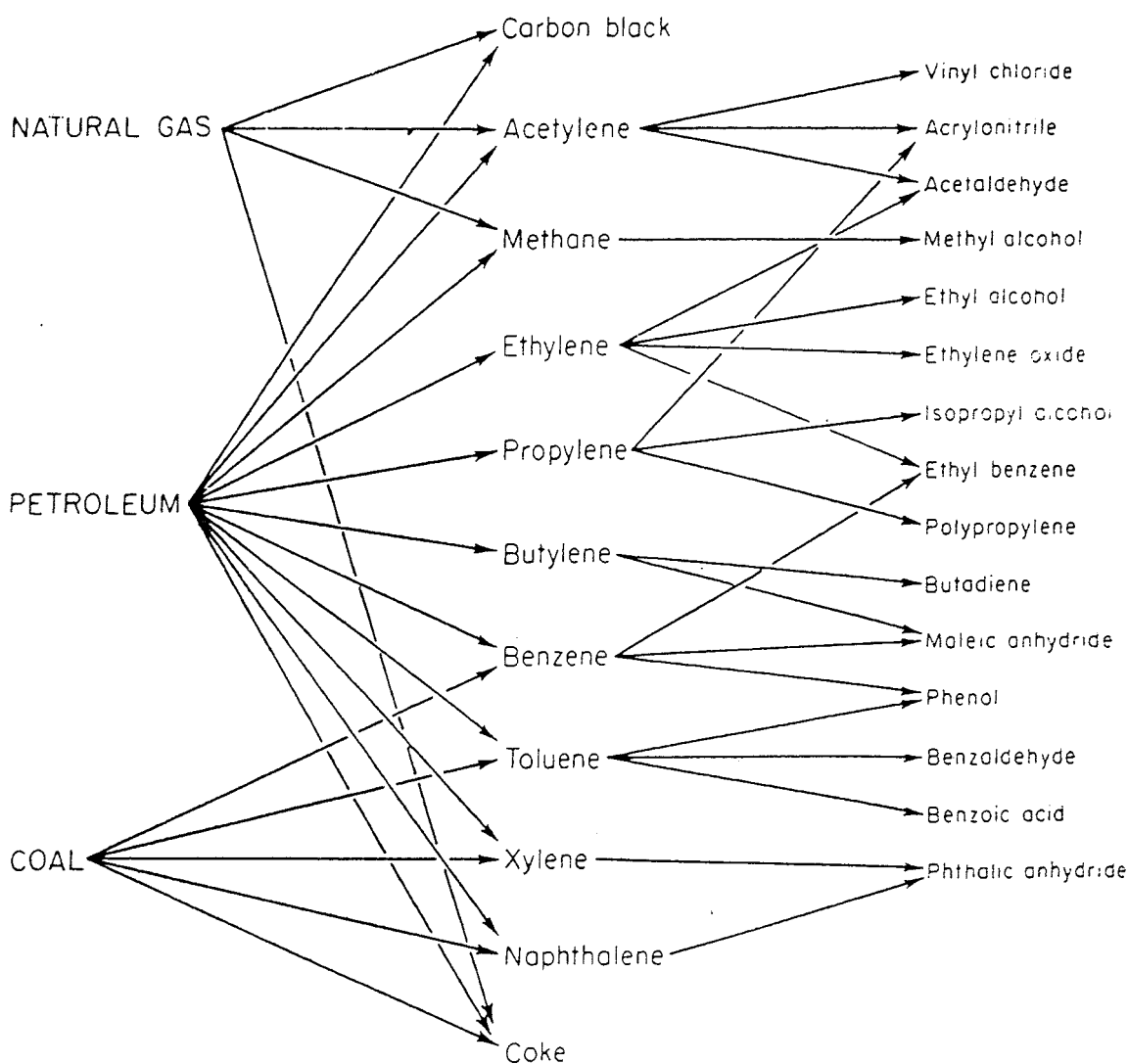


Fig. 37.6. Interrelationship of precursors from natural gas, petroleum cuts, and coal. (Marshall Sittig.)

3.13×10^7 kg/year. Dealkylation of a selected reformate stream using chromate-aluminum carbide catalyst with a 10-s exposure gives a product which is purified to be purer than that formed from coal tar. The Hydeal process by Ashland Oil Co. is one of the processes used.

LIGHT DISTILLATES. Aviation gasoline, (automobile) motor gasoline, naphthas, petroleum solvents, jet-fuel, and kerosene are the fractions generally regarded as light distillates. Any given refinery rarely makes all of them. Gasoline is the most important product, and around 45 percent of the crude processed now ends up as gasoline. When the compression ratio of a motor is relatively high, the fuel can detonate in the cylinder causing noise (knock), power loss, and ultimately engine damage. Branched chain and aromatic hydrocarbons greatly reduce the tendency of a fuel to cause knocking. *n*-Heptane knocks very readily; 2,2,4-trimethyl pentane (formerly known as iso-octane) is an extremely antiknock fuel. The *octane number*, a measure of the suitability of a fuel for high-compression engines, is the percentage of iso-octane which, when added to *n*-heptane, knocks in a special test engine to the same degree as the fuel being tested. Certain substances, such as tetraethyl lead (TEL) and tetramethyl lead (TML) can be added to gasoline in very small quantities to raise the octane number dramatically. Because of doubts concerning the safety of lead in the environment, these most useful additives are now restricted or limited. Cleaner burning is achieved by adding intake system detergents.

Aviation gasoline is generally sold in two grades, 100 octane and 80 octane with the major demand for 100 octane. Some compounds or mixtures are now known which either have octane numbers above 100, or blend as if they had numbers over 100, so avgas is a blend of catalytically cracked gasoline, high-quality alkylate, and TEL.

The amount of sulfur that can safely be permitted in gasoline is debatable, but sulfur is always undesirable. Concentrations as high as 0.2% do not cause serious corrosion, but regulations usually limit sulfur to around 0.1%. TEL effectiveness is sharply reduced by the presence of sulfur or sulfur compounds.

When the Environmental Protection Agency (EPA) reduced the lead (as TEL) allowable in some gasoline and required its absence from most, refineries faced a difficult problem. The amount of branched chain and aromatic constituents in regular gasoline had to be increased to keep the antiknock high after the lead was removed. The problem was resolved by utilizing more severe cracking, by adding octane boosters such as methyl tertiary butyl ether (MTBE), methanol, and ethanol. This continues to be a problem for gasoline suppliers.

Originally, water whiteness in gasoline was an indication of good quality distillation, but this hasn't been true for nearly 50 years. Consumers still prefer clear colorless products, but it is expensive and pointless to produce them. Oil-soluble dyes are now added to give uniformity of color and to identify the company from which the fuel came.

The term *naphtha* is loosely applied to materials with boiling ranges between gasoline and kerosene. There are a number of specialty naphthas, e.g. varnish maker's and painter's naphtha (VM&P), dry cleaning solvent, rubber solvent, etc. Some naphthas are used for ethylene feedstocks, but the cost is high and the use diminishing. The military uses a naphtha-based jet-fuel known as JP-4 extensively.

Kerosene was originally used for lamps and home heating, but most is now used as jet fuel for airplanes.

INTERMEDIATE DISTILLATES. These include gas oil, light and heavy domestic furnace oils, diesel fuels, and distillates used for cracking to produce more gasoline. These distillates are used mainly for transportation fuels in heavy trucks, railroads, small commercial boats, standby and peak-shaving power plants, farm equipment, and wherever diesels are used to produce power. Home heating furnaces use these distillates. Asphalt is "cut back," i.e., made less viscous, with them. The name gas oil originated with their use to produce illuminants to improve the lighting value of manufactured town gas; this use has disappeared. The heavier grades are especially suited for cracking to produce motor gasoline. Yields of gasoline as high as 1.08 L per liter of distillate fed are obtained. The major volume goes into diesel fuel.

ADDITIVES TO PETROLEUM PRODUCTS.²⁴ Doubts concerning their environmental effects have reduced the use of additives which have often produced large improvements in performance with tiny additions. In 1972, the use of TEL/TML was over 440×10^6 kg, but by 1982 it had fallen to 143×10^6 kg; it is projected to fall to 91×10^6 kg by 1986. Unleaded gasolines require more alkylates and reformates to maintain their quality. Organophosphates reduce combustion chamber deposits, but their use is also restricted. Corrosion inhibitors are used, and in some cases antioxidants to stabilize the olefins and diolefins, thus reducing the production of engine gum and varnish. Detergents are added to gasoline and lubricating oils

²⁴Miles, *Chemical Additives for Fuels*, Noyes, Park Ridge, N.J., 1982; Ranney, *Corrosion Inhibitors*, Noyes, Park Ridge, N.J., 1976; Fuel and Lubricant Additives, I and II, *Lubrication* 63 (1 and 2), Texaco Co., 1977; Satriana (ed.), *Synthetic Oils and Lubricant Additives since 1979*, Noyes, Park Ridge, N.J., 1982.